Pre-eminence of the Indirect Channel in the Resonant Inverse Photoelectron Spectroscopy of Cerium Oxide

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Pre-eminence of the Indirect Channel in the Resonant Inverse Photoelectron Spectroscopy of Cerium Oxide[a]

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Abstract

A strong resonance in the inverse photoelectron spectroscopy (IPES) of Cerium Oxide was

reported recently. [1] Here, it is shown that dominance of the indirect channel of the resonant

inverse photoelectron spectroscopy (RIPES) is so complete that the photon energy

dependence can be explained in terms of emission from a single photon energy.

Materials terms:

Cerium, Oxygen, Soft X-ray Spectroscopy

Pre-eminence of the Indirect Channel in the Resonant Inverse Photoelectron Spectroscopy of Cerium Oxide[a]

I   Introduction

Soft X-ray spectroscopy provides a powerful approach for the interrogation of the electronic structure of materials and surfaces. Three particularly important variants are inverse photoelectron spectroscopy (IPES) [1], X-ray emission spectroscopy (XES) [1], and X-ray absorption spectroscopy (XAS) [2]. Examples of the data for each are shown in Figure 1. Diagrams of the underlying processes are illustrated in Figure 2. In the case of inverse photoelectron spectroscopy, also known as Bremstrahlung Isochromat Spectroscopy (BIS) at high energies, it is possible to operate under resonant conditions (RIPES), where a second, indirect channel can contribute to the intensity, analogous with resonant photoelectron spectroscopy (RESPES) [3]. The indirect channel involves going through a core level with the concomitant requirement that the direct and indirect channels end with the same final state [1,3]. In the case of the Ce3d levels, of Cerium Oxide, the resonance is extraordinarily strong and the indirect channel is overwhelmingly pre-eminent, as will be shown below.

II   Experimental

The XES and RIPES experiments were carried out at Lawrence Livermore National Laboratory (LLNL), as described elsewhere [1]. The XAS measurements were made on Beam-line 8 at the Advance Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL), in Berkeley, CA [2].

III   Spectral Results and Discussion

Shown in Figure 1 are the XAS, XES, and RIPES of Cerium Oxide. There are two key points that can be derived from this collection of spectra. First, the RIPES lies under the Ce3d5/2 peak of the Cerium Oxide, not the cerium metal. Second, despite the fact that the

Pre-eminence of the Indirect Channel in the Resonant Inverse Photoelectron Spectroscopy of Cerium Oxide[a]

RIPES is associated with Cerium Oxide, the RIPES has a Fermi Level. The issue of the relative placement of the Cerium metal and Cerium Oxide peaks is discussed in detail in References 1 and 2. Here, it is sufficient to note that for both XAS and XES, the Cerium Oxide peaks occur at higher photon energies that than the corresponding Cerium metal peaks. The presence of a Fermi Level is a Cerium Oxide layer on top of a Cerium metal substrate has been observed before [4], as described in Reference 1. As illustrated in Figure 3, the sharp rise on the high photon energy side of the RIPES peak is clearly a Fermi Edge, with a width of 1.6 eV [5].

The photon energy dependence of the RIPES of the Ce3d5/2 level of Cerium Oxide is shown in Figure 4. Outside of the resonance range, it is very difficult to observe an IPES peak above the background noise. In the resonance range of 879 eV to 885 eV, essentially all of the spectral intensity fits inside the maximally resonant feature at hv = 881 eV. There is little, if any, intensity above the Fermi Edge of the hv = 881 eV spectrum. Note again that this Fermi edge falls below the Cerium Oxide peak and, in fact, the top end of the Fermi Edge is well aligned with the center if this same XES peak.

As shown in Figure 5, a similar situation holds for the RIPES near the Ce3d3/2 XES feature. Here, the resonance is near hv = 899-900 eV and all of the resonance intensity falls within the envelope of the hv = 899 eV and hv = 900 eV RIPES spectra. The Ce3d3/2 result is degraded relative to the Ce3d5/2 result by two connected effects. The Ce3d3/2 features, both XES and RIPES, exhibit a greater width, probably driven by lifetime broadening. In general, the l-1/2 peaks are broader that l+1/2 peaks in spin-orbit-split pairs. This is caused by the rapid decay process of filling the deeper l-1/2 hole by an electron from the shallower l+1/2 level. This process is shown in Figure 2. Another result of this process is the effective

Pre-eminence of the Indirect Channel in the Resonant Inverse Photoelectron Spectroscopy of Cerium Oxide[a]

transfer of intensity from the 3d3/2 peak to the 3d5/2 peak, as discussed in detail in Reference 1 and illustrated in the insert in Figure 5. Regardless of this degradation, the underlying trend in the photon energy dependence of the 3d3/2 RIPES is the same as that of the 3d5/2 RIPES: All of the intensity is inside the envelope of the main resonant RIPES spectrum, either hv = 899/900 eV or hv = 881 eV, respectively.

A qualitative understanding of this phenomenon can be garnered considering the schematic in Figure 6. The intersection of the direct IPES channel, dispersing linearly with photon energy, and the indirect channel of the main resonant peak, fixed in photon energy, is plotted herein. It is proposed here that the overlap of the plots of these two channels can explain what is observed in Figure 4 and 5. While the peak shapes in Figure 6 are simplistically represented as triangles, nevertheless the correct trends are observed. All of the intensity falls within the main resonant feature, first rising and then dropping with increasing photon energy. Clearly, in real systems, peaks are neither triangular nor even symmetric. The wider wings of Lorentzian peak-shapes [6] and asymmetric tails of Doniac-Sunjic line-shapes [7] can easily explain some of the complications observed in Figures 4 and 5, relative to Figure 6. It is also important to note that the dominance of the indirect channel is not universal. Dispersal of the IPES features has been observed often, including off-resonance dispersion at low energies [8] and on resonance for Uranium [9] and Uranium Dioxide [10].

IV   Conclusions

It has been shown that the strongly resonant case of the RIPES of the Ce3d5/2 and Ce3d3/2 levels of Cerium Oxide can be explained by an almost complete dominance of the indirect channel of the main resonant photon energy.

Pre-eminence of the Indirect Channel in the Resonant Inverse Photoelectron Spectroscopy of Cerium Oxide[a]

Acknowledgements

References

1. J.G. Tobin, S.W. Yu, B.W. Chung, G.D. Waddill, E. Damian, L. Duda and J. Nordgren, Phys. Rev B **83**, 085104 (2011).

2. J.G. Tobin, S.-W. Yu, B.W. Chung, G.D. Waddill and J.D. Denlinger, J. Vac. Sci. Tech. **A 29,** 031504 (2011).

3. S.R. Mishra, T.R. Cummins, G. D. Waddill, W.J. Gammon, G. van der Laan, K.W. Goodman, and J.G. Tobin, Phys. Rev. Lett. **81**, 1306 (1998).

4. B.W. Veal and D. J. Lam, Phys. Rev. B **10**, 4902 (1974); Phys. Lett.A **49**, 466 (1974).

5. S.-W. Yu, J. G. Tobin, and B. W. Chung**,** Rev. Sci. Instruments **82**, 093903 (2011).

6. S.-W. Yu, J. G. Tobin, J. C. Crowhurst, S. Sharma, J. K. Dewhurst, P. Olalde-Velasco, W. L. Yang, and W. J. Siekhaus, Phys. Rev. B **83**, 165102 (2011).

7. J.G. Tobin and F.O. Schumann, Surface Science **478**, 211 (2001).

8. B. Knapp and J. Tobin, Phys. Rev. B **37**, 8656 (1988).

9. M. Grioni et al., J. Electron Spectrosc. Relat. Phenom. 101−103, 713 (1999).

10. J.G. Tobin and S.-W. Yu, Phys. Rev. Lett, **107,** 167406 (2011).

Pre-eminence of the Indirect Channel in the Resonant Inverse Photoelectron Spectroscopy of Cerium Oxide[a]

Figure Captions

Figure 1   The XAS, XES and RIPES at hv = 881 eV are plotted here. (a) The XAS of Cerium metal, Cerium Oxide on Cerium metal and reference spectra of a thin film of Cerium Oxide [2]. The instrumental broadening of the XAS is on the scale of 0.1 eV to 0.2 eV, allowing for the observation of substantial fine structure. TEY is total electron yield. TYF is total fluorescence yield. (b) The XES and RIPES of Ce Oxide/Ce metal sample [1]. The instrumental resolution is on the scale of about 2 eV for the RIPES and less than 2 eV for the XES. This broader instrumental band-pass contributes to the loss of fine structure relative to XAS.

Figure 2   This is a schematic illustrating the essentials of the processes for XAS, XES and RIPES of the Ce3d5/2 and Ce3d3/2 levels. Non-resonant IPES or BIS would correspond to the direct channel in RIPES. H^F is the energy of the hole to be filled in RIPES or IPES, relative to the Fermi Level. ϕ is the work function. KE is kinetic energy. hv is photon energy. B^F is the binding energy of the electron relative to the Fermi Level. CB is conduction band. VB is valence band. $\Delta(VB)$ and $\Delta(CB)$ are the small effective offsets in XAS and XES, respectively, as described in Reference 2.

Figure 3   (a) The raw RIPES data at KE = 881 eV, including the underlying detector background. (b) Detail of the KE = 881 eV spectrum, including the Fermi Edge 10%-90% width, which is equivalent to the Full-Width-at Half-Maximum (FWHM) peak width. H^F is defined in Figure 2. Note the sharpness of the Fermi Edge.

Pre-eminence of the Indirect Channel in the Resonant Inverse Photoelectron Spectroscopy of Cerium Oxide[a]

Figure 4   An expanded view of the RIPES and XES of the Ce3d5/2 level of Cerium

Oxide. For each excitation KE, the raw spectrum corresponding to panel (b) in

Figure 3 is plotted. Only one constant background has been subtracted for all

of the spectra at different KE's. Note the Fermi Edge at a photon-energy of

about 883 eV.

Figure 5   The same as Figure 4, but for the Ce3d3/2 level of Cerium Oxide. The inset

shows a wider range plot of the same data.

Figure 6   A diagram showing the intersection (black) of the direct channel (red) and the

indirect channel (blue) of the main resonance. The indirect channel is at a

fixed photon energy. The photon energy of the direct channel disperses

linearly with the excitation KE, as defined in Figure 2.   The observed peaks

(black) all fall inside the boundaries defined by the indirect channel. See text

for discussion. The experimental peaks which would correspond to hv = 878

eV and 896 eV appear to be lost in the background, perhaps due to peak

asymmetry in the experimental data in Figures 4 and 5.
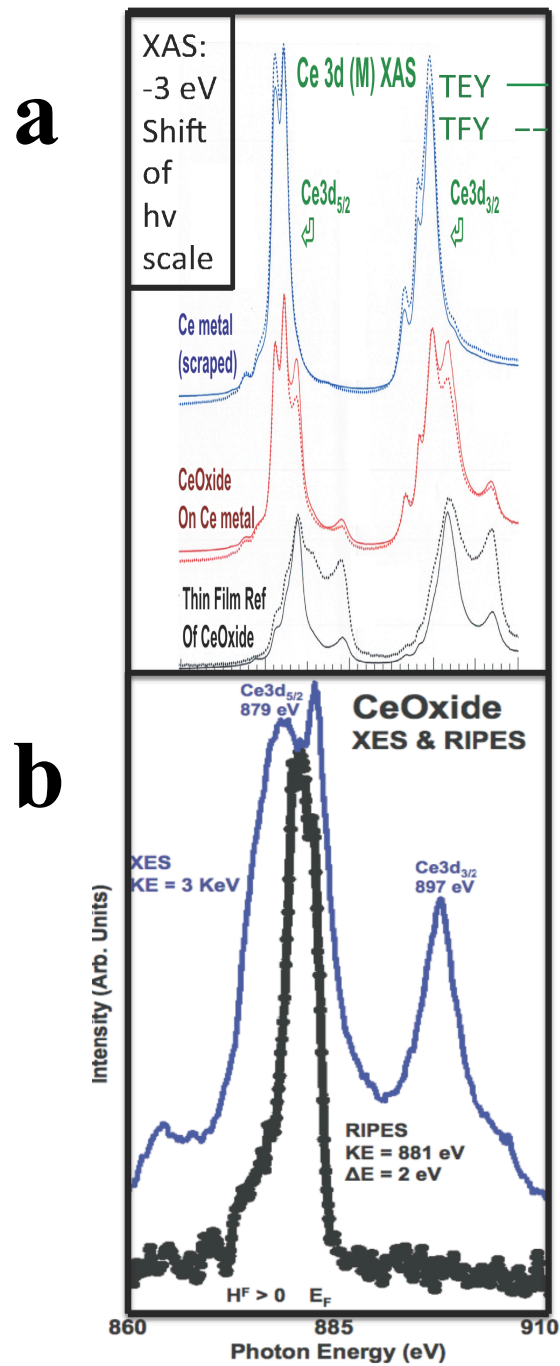
Figure 1

Pre-eminence of the Indirect Channel in the Resonant Inverse Photoelectron Spectroscopy of Cerium Oxide[a]

Figure 2

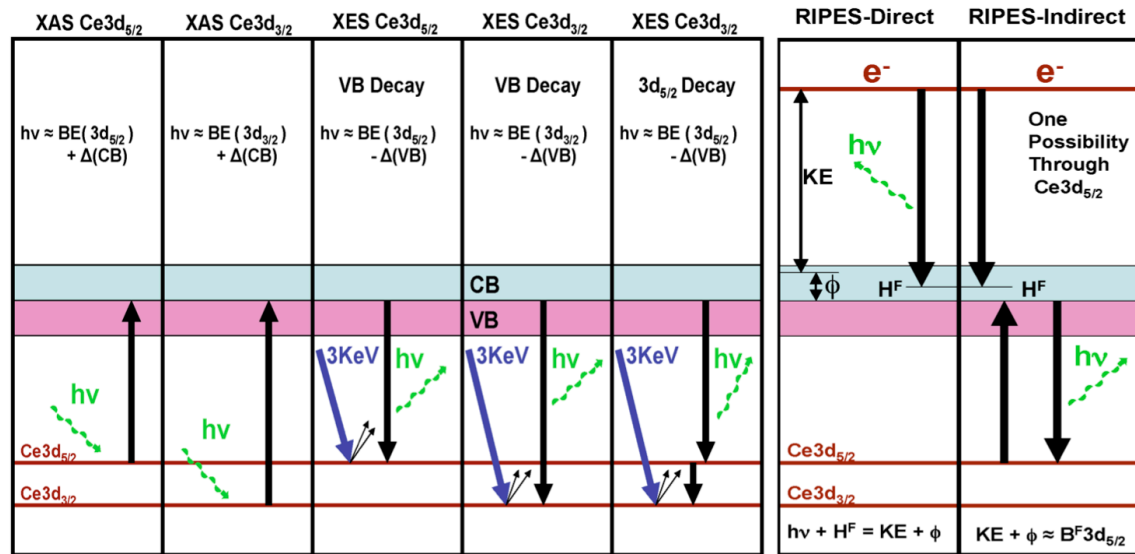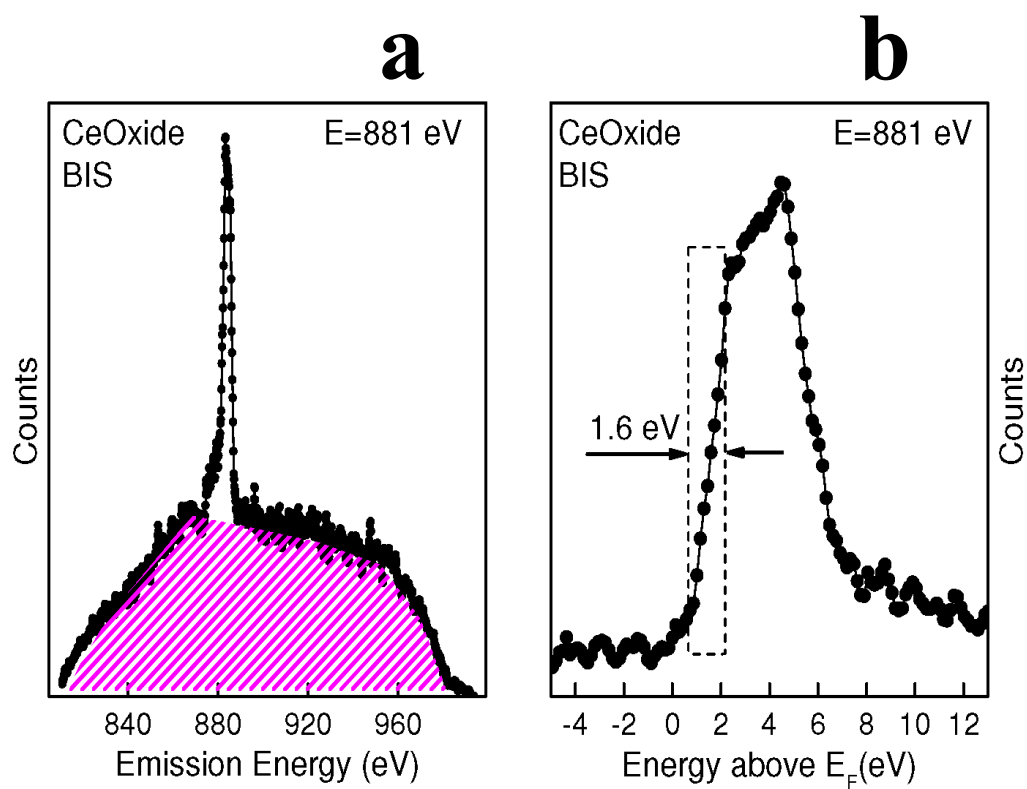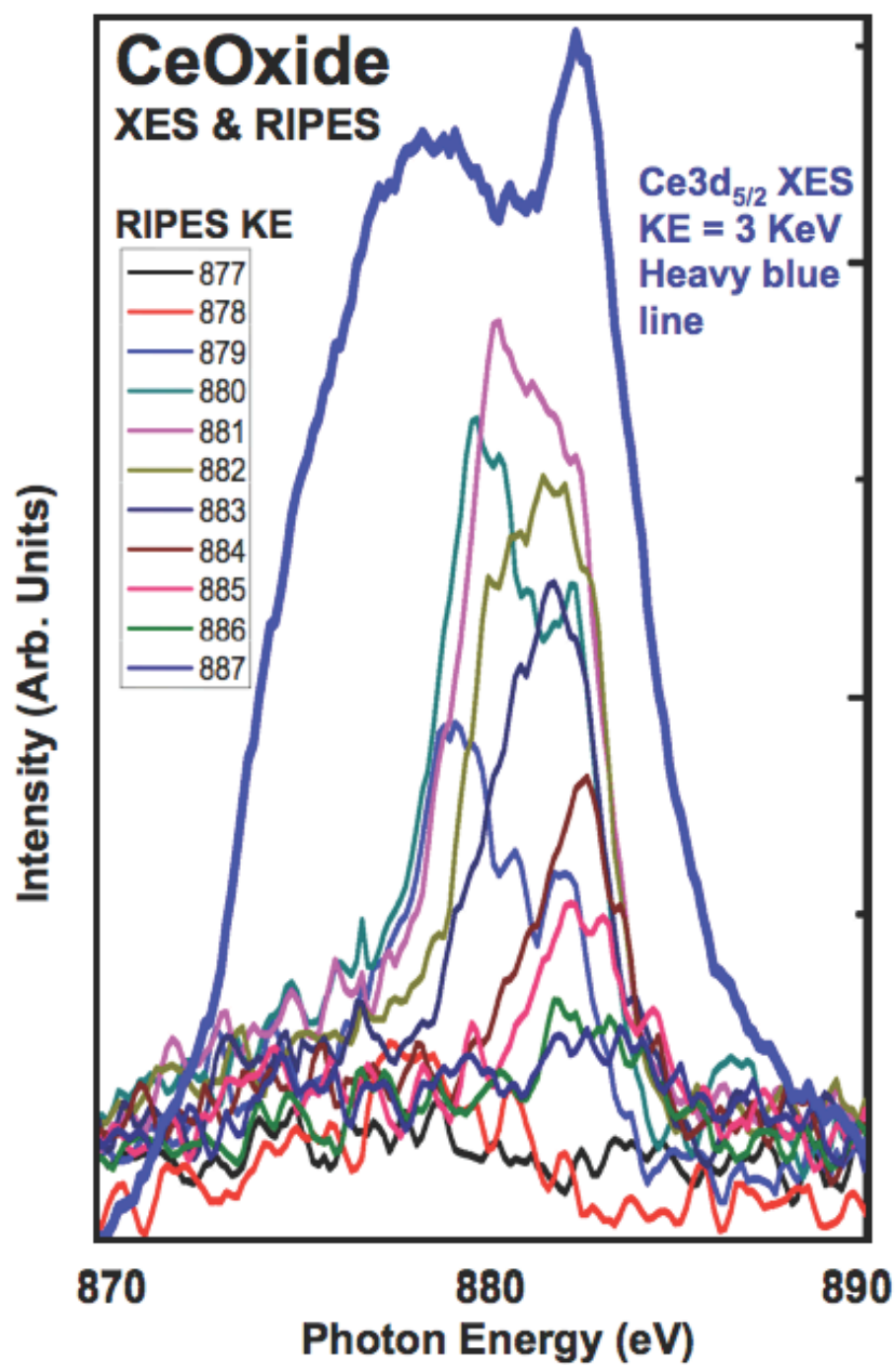# Pre-eminence of the Indirect Channel in the Resonant Inverse Photoelectron Spectroscopy of Cerium Oxide[a]

a

CeOxide
BIS

E=881 eV

Counts

840   880   920   960

Emission Energy (eV)

b

CeOxide
BIS

E=881 eV

1.6 eV

Counts

-4 -2   0   2   4   6   8 10 12

Energy above E_F(eV)

Figure 3

Pre-eminence of the Indirect Channel in the Resonant Inverse Photoelectron Spectroscopy of Cerium Oxide[a]

Figure 4

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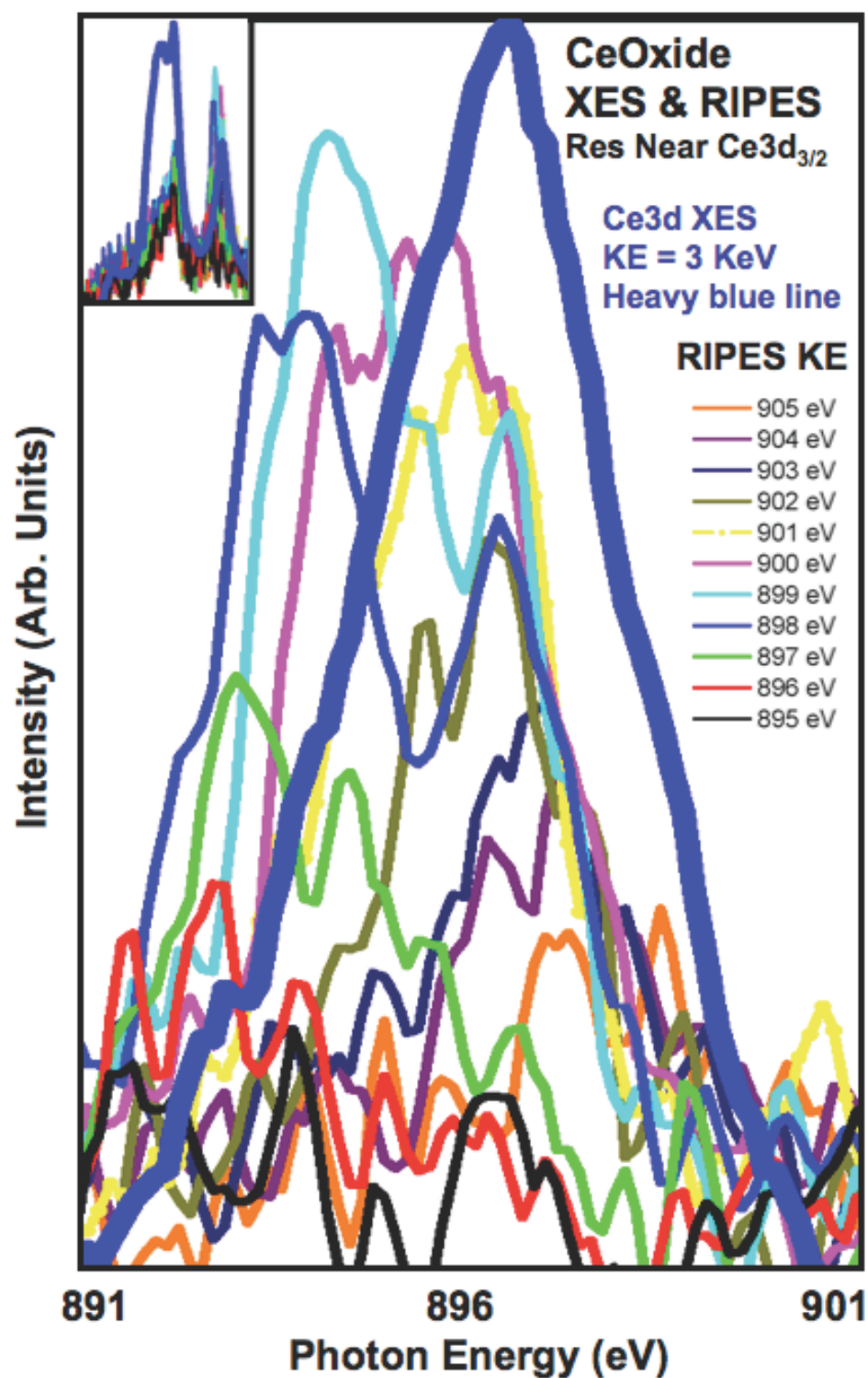

Figure 5

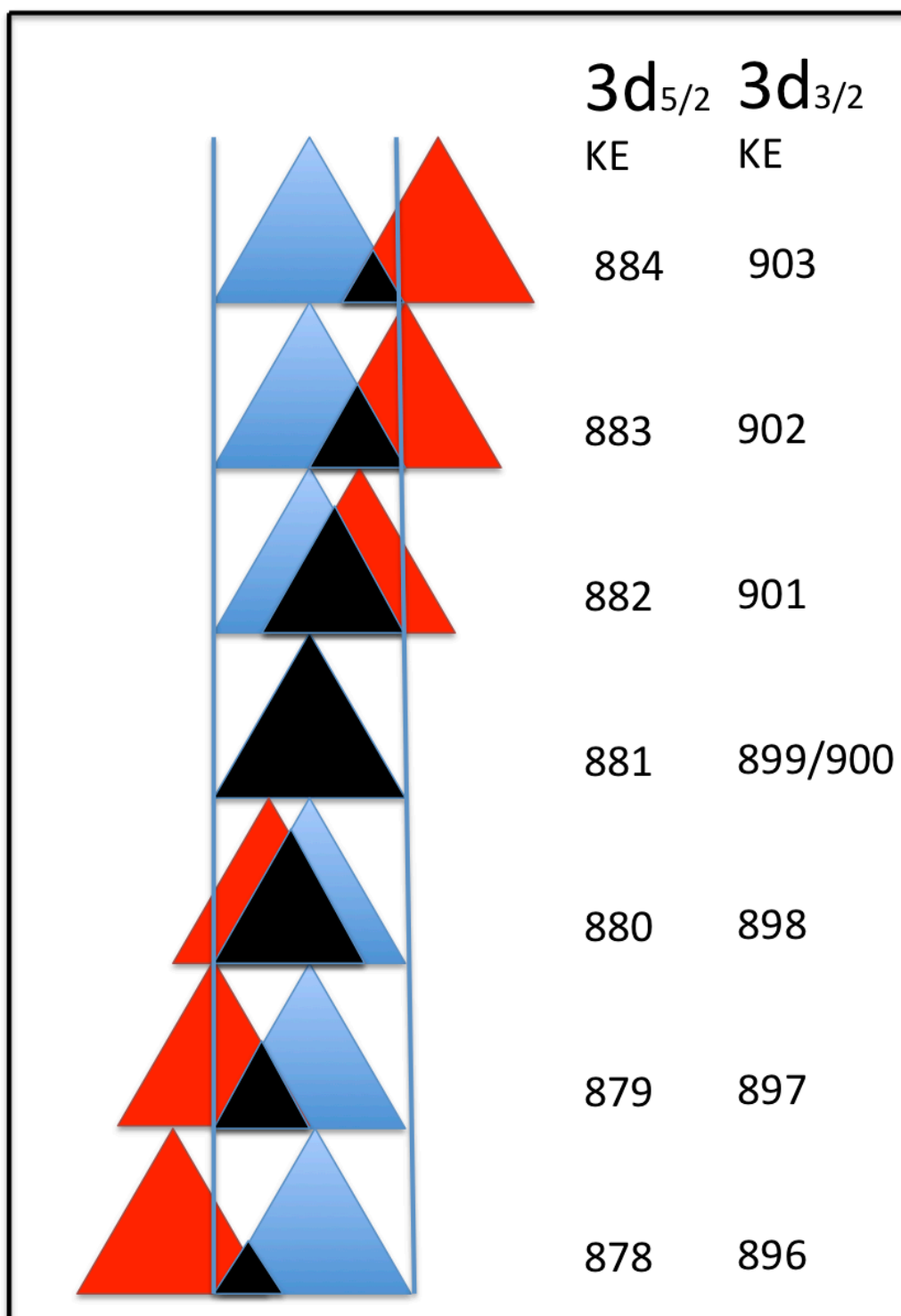# Pre-eminence of the Indirect Channel in the Resonant Inverse Photoelectron Spectroscopy of Cerium Oxide[a]

Figure 6